PATENT ABSTRACTS OF JAPAN

(11)Publication number : 06-176794
(43)Date of publication of application : 24.06.1994

(51)Int.Cl. H01M 10/40
H01M 4/58

(21)Application number : 04-327653
(22)Date of filing : 08.12.1992

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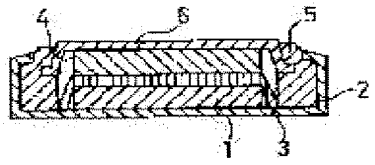
(54) NONAQUEOUS ELECTROLYTE SECONDARY BATTERY

(57)Abstract:
PURPOSE: To provide a nonaqueous electrolyte secondary battery of high energy density.
CONSTITUTION: For a nonaqueous electrolyte secondary battery which consists of a charge and discharge allowable positive electrode 1, nonaqueous electrolyte and a charge and discharge allowable negative electrode 4, a BC3 electrode is used as the positive electrode 1. By using the BC3 electrode, the nonaqueous electrolyte secondary battery is excellent in high voltage, high capacity and reservation property.



LEGAL STATUS

[Date of request for examination] 07.10.1998
[Date of sending the examiner's decision of rejection] 10.04.2001
[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]
[Date of final disposal for application]
[Patent number]
[Date of registration]
[Number of appeal against examiner's decision

of rejection]
[Date of requesting appeal against examiner's decision of rejection]
[Date of extinction of right]

* NOTICES *

CLAIMS

[Claim(s)]
[Claim 1] It is a nonaqueous electrolyte rechargeable battery possessing the positive electrode in which charge and discharge are possible, nonaqueous electrolyte, and the negative electrode in which charge and discharge are possible, and the aforementioned positive electrode is BC3. Nonaqueous electrolyte rechargeable battery which consists of an electrode.

[Translation done.]

* NOTICES *

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] this invention relates to a nonaqueous electrolyte rechargeable battery with the positive electrode made into high-energy density.
[0002]
[Description of the Prior Art] Until now, it is ********** about attention as an electrode material of a nonaqueous electrolyte rechargeable battery since a carbon material has oxidation reduction behavior in conductive polymer rows, such as the poly aniline, the poly acene, a polyacethylene, polypyrrole, and the poly thiophene. When it excels in flexibility and a metal lithium is used especially for a negative electrode, it is known that these electrode materials are lightweight and that it may become a high voltage and a high-energy density cell. When these material is used for a positive electrode, the anion in the electrolytic solution is incorporated at the time of charge, and an anion is conversely emitted at the time of electric discharge. If quantity of electricity per unit weight shows, the material which reaches a maximum of 200 mAh/g also exists. The nonaqueous electrolyte rechargeable battery is commercialized as having made especially the poly aniline into the positive electrode.
[0003]
[Problem(s) to be Solved by the Invention] However, when a nonaqueous electrolyte rechargeable battery does not consist of only these material but the other materials, such as the electrolytic solution, are taken into consideration, it is not necessarily no longer high-energy density. Moreover, that the specific gravity of these material is low makes the energy density per volume fall sharply conversely. Moreover, when a cycle life was taken into consideration, charge and discharge needed to be carried out more considerably than geometric capacity in the low portion. For this reason, in order to obtain the nonaqueous electrolyte rechargeable battery of high-energy density, a still high capacity positive electrode is needed.
[0004] this invention aims at improving a positive electrode with careful attention to the aforementioned conventional problem, and offering the nonaqueous electrolyte rechargeable battery of high-energy density.
[0005]
[Means for Solving the Problem] It sets to the positive electrode in which charge and discharge are possible in order to attain the above-mentioned purpose, nonaqueous electrolyte, and the nonaqueous electrolyte rechargeable battery possessing the negative electrode in which charge and discharge are possible, and this invention is BC3 to the aforementioned positive electrode. It considers as the used composition.
[0006]
[Function] Above BC3 Electrical conductivity is higher than a graphite 10%. Therefore, BC3 When it uses for the positive electrode of a nonaqueous electrolyte rechargeable battery, an electric conduction agent becomes unnecessary. Moreover, specific gravity is the same as a graphite at 2.2. BC3 The boron (B) to constitute has one electron in 2S orbit at two pieces and 2P orbit, and carbon has two electrons in 2S orbit at two pieces and 2P orbit. Therefore, compared with carbon, one electron is scarce.

[0007] It is BC3 here. If a positive electrode is charged in nonaqueous electrolyte, if occlusion of the anion is carried out all over a positive electrode and it discharges, the anion by which occlusion was carried out will be emitted into the electrolytic solution like [a conductive polymer row] a carbon material. And as for the average discharge voltage at that time, service capacity also serves as 210 mAh/g by 4.5V to Li pole. Thus, it is BC3 to a positive electrode. By using, a high voltage nonaqueous electrolyte rechargeable battery can be offered by high capacity.
[0008]
[Example] The example of this invention is explained below.
(Example 1) BC3 In order to examine the property as an electrode, the coin type nonaqueous electrolyte rechargeable battery shown in drawing 1 was made.
[0009] 1g of poly ethylene tetrafluoride was first mixed as a binder to BC3 10g, and it considered as the mixture. Pressurization molding of the 0.1g of this mixture is carried out at the diameter of 17.5mm, and it is BC3. It was referred to very much as 1, and placed into the case 2. It is BC3 about the microporosity polypropylene separator 3. It placed on one very much. It poured in on separator 3 by making into nonaqueous electrolyte the propylene carbonate (PC) which dissolved the lithium perchlorate (LiClO4) of 1 mol / 1. Besides, the metal Li4 with a diameter of 17.5mm was stuck inside, the obturation board 6 which attached the polypropylene gasket 5 to the periphery section was placed and obturated, and the coin type nonaqueous electrolyte rechargeable battery was produced.
[0010] Next at a 2mA constant current, it is BC3. Anode polarization (equivalent to charge, when seeing BC3 electrode as a positive electrode) is carried out until an electrode 1 is set to 4.7V to the Li counter electrode 4, and next, it is BC3. Cathode polarization (equivalent to electric discharge) was carried out until the electrode 1 was set to 3.0V. And it carried out by repeating this anode polarization and cathode polarization.
[0011] As a conventional example, the poly aniline is used for a vapor-growth carbon-material row, and it is BC3. It carried out by producing an electrode as well as an electrode, making an examination cell like a degree, and repeating anode polarization and cathode polarization. The electrode which used the poly aniline for the vapor-growth carbon-material row after that is abbreviated to C electrode and P electrode. In addition, about P electrode, anode polarization (equivalent to charge, when seeing as a positive electrode) was carried out until it was set to 4.0V to Li counter electrode, and cathode polarization (equivalent to electric discharge) was carried out until P electrode was set to 3.0V next. And it carried out by repeating this anode polarization and cathode polarization.
[0012] It is BC3 to a positive electrode. The charge-and-discharge curve of 1 cycle eye of the nonaqueous electrolyte rechargeable battery using the electrode, C electrode, and P electrode is shown in drawing 2 . Moreover (Table 1), the capacity maintenance factor of the service capacity of the nonaqueous electrolyte rechargeable battery of a 100 cycle eye to initial service capacity and initial service capacity is shown.
[0013]
[Table 1]

正　　極	放電容量（ｍＡｈ／ｇ）	１００サイクル目の放電容量維持率（％）
BC_3	２１０	９７
C	７５	９２
ポリアニリン	１４８	８９

[0014] Discharge voltage is BC3. The thing using the electrode as a positive electrode is higher than what used P electrode for C electrode row, and electric capacity is also BC3 of this example. It turns out that the thing using the electrode is as large as 210 mAh/g. Moreover, also

service-capacity maintenance factor BC3 of a 100 cycle eye The thing using the electrode showed the highest value.
(Example 2) In this example, it investigated about the elevated-temperature preservation property.
[0015] BC3 The coin type nonaqueous electrolyte rechargeable battery shown in drawing 1 made into a positive electrode was constituted. Moreover, as a conventional example, the poly aniline is used for a vapor-growth carbon-material row, and it is BC3. The coin type non-water electrolysis rechargeable battery which made the positive electrode C electrode and P electrode as well as an electrode was produced. The method of producing the aforementioned cell was performed by the same method as an example 1.
[0016] The elevated-temperature retention test of a nonaqueous electrolyte rechargeable battery was performed by the following method. It is BC3 at a constant current (20 degrees C and 2mA). Next, about what used P electrode to 4.7V about the thing using the electrode and C electrode, it charged to 4.0V, and any nonaqueous electrolyte rechargeable battery discharged to 3.0V, and this charge and discharge were saved for three weeks at 60 degrees C, after 5 cycle deed and charge of 6 cycle eye finished. It returned to 20 degrees C after preservation, and discharged on these conditions. The capacity maintenance factor was defined as follows here.
[0017] Capacity maintenance factor = it charged after the service capacity of the service capacity / 5 cycle eye of a 100x6 cycle eye, and the preservation end, and subsequent service capacity was evaluated. The capacity recovery factor was defined as follows here.
[0018] Capacity recovery factor = the capacity maintenance factor three weeks after each nonaqueous electrolyte rechargeable battery and a capacity recovery factor are shown in the service capacity (Table 2) of the service capacity / 5 cycle eye of a 100x7 cycle eye.
[0019]
[Table 2]

正　　極	5ｻｲｸﾙ目放電容量（ｍＡｈ／ｇ）	容量維持率（％）	容量回復率（％）
BC_3	２０９	９０	９６
C	７４	８２	９３
ポリアニリン	１４５	６２	８５

[0020] BC3 The nonaqueous electrolyte rechargeable battery using the electrode has the largest capacity recovery factor compared with the nonaqueous electrolyte rechargeable battery which used C electrode and P electrode in a capacity maintenance-factor row. Thus, the nonaqueous electrolyte rechargeable battery of this example is BC3. By having used the electrode as a positive electrode showed having had high discharge voltage, high capacity, and the outstanding preservation property.
[0021] In addition, although the coin type nonaqueous electrolyte rechargeable battery explained in each example, it does not change with configurations, such as cylindrical and a square shape.
[0022]
[Effect of the Invention] this invention is set to the nonaqueous electrolyte rechargeable battery possessing the positive electrode in which charge and discharge are possible, nonaqueous electrolyte, and the negative electrode in which charge and discharge are possible so that more clearly than explanation of the above example, and it is BC3 to the aforementioned positive electrode. Since it used, it is high-energy density, and the rechargeable battery excellent in shelf life can be obtained, and the meaning on industry is large.

[Translation done.]

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] The cross section of the coin type nonaqueous electrolyte rechargeable battery using the positive electrode of this invention
[Drawing 2] The charge-and-discharge curve view in the coin type nonaqueous electrolyte rechargeable battery using the positive electrode of this invention in comparison with the conventional example
[Description of Notations]
1 Electrode (Positive Electrode)
2 Case
3 Separator
4 Metal Li
5 Gasket
6 Obturation Board

[Translation done.]

(19)日本国特許庁（ＪＰ）　(12) **公開特許公報**（Ａ）　(11)特許出願公開番号

特開平6－176794

(43)公開日　平成6年(1994)6月24日

(51)Int.Cl.[5]	識別記号	庁内整理番号	ＦＩ	技術表示箇所
Ｈ０１Ｍ　10/40		Ｚ		
4/58				

審査請求　未請求　請求項の数１（全　４　頁）

(21)出願番号　特願平4－327653

(22)出願日　平成４年(1992)12月８日

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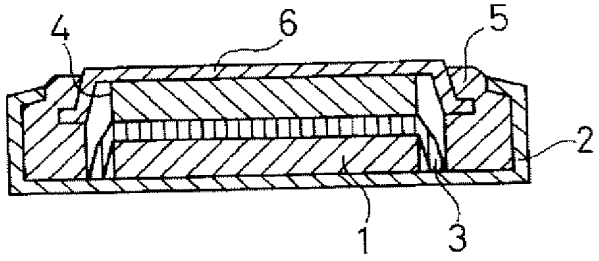
(54)【発明の名称】　非水電解液二次電池

(57)【要約】
【目的】高エネルギー密度非水電解液二次電池を提供することを目的とする。
【構成】充放電可能な正極１と、非水電解液と、充放電可能な負極４を具備する非水電解液二次電池において、前記正極１にBC_3電極を用いる構成とする。
【効果】前記BC_3正極を用いることで、高電圧、高容量ならびに保存性に優れた非水電解液二次電池を得ることができる。



1----電極(正極)
2----ケース
3----セパレータ
4----金属Li
5----ガスケット
6----封口板

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【特許請求の範囲】
【請求項１】　充放電可能な正極と、非水電解液と、充放電可能な負極を具備する非水電解液二次電池であって、前記正極がBC_3電極よりなる非水電解液二次電池。
【発明の詳細な説明】
【０００１】
【産業上の利用分野】本発明は高エネルギー密度にする正極をもつ非水電解液二次電池に関する。
【０００２】
【従来の技術】これまでに、ポリアニリン、ポリアセン、ポリアセチレン、ポリピロール、ポリチオフェンなどの導電性高分子ならびに炭素材料は、酸化還元挙動を有することから、非水電解液二次電池の電極材料として注目をあつめてきた。これら電極材料は、軽量かつ可とう性に優れ、特に負極に金属リチウムを用いた場合、高電圧、高エネルギー密度電池となりうることが知られている。これら材料を正極に用いた場合、充電時に電解液中のアニオンを取り込み、逆に放電時にアニオンを放出する。単位重量当りの電気量で示すと、最高２００ｍＡｈ／ｇに達する材料も存在する。特にポリアニリンを正極としたと非水電解液二次電池は商品化されている。
【０００３】
【発明が解決しようとする課題】しかし、これら材料だけで非水電解液二次電池は構成されるのではなく、電解液などその他の材料を考慮すると、必ずしも高エネルギー密度ではなくなる。またこれら材料の比重の低いことは、逆に体積当りのエネルギー密度を大幅に低下させることになる。またサイクル寿命を考慮した場合、理論容量よりもかなり低い部分で充放電する必要があった。このため高エネルギー密度の非水電解液二次電池を得るためにはさらに高容量な正極が必要となる。
【０００４】本発明は前記従来の問題に留意し正極を改良して高エネルギー密度の非水電解液二次電池を提供することを目的とする。
【０００５】
【課題を解決するための手段】本発明は、上記目的を達成するために、充放電可能な正極と、非水電解液と、充放電可能な負極を具備する非水電解液二次電池において、前記正極にBC_3を用いた構成とする。
【０００６】
【作用】前記BC_3の電気伝導度は、黒鉛より１０％高い。したがってBC_3を非水電解液二次電池の正極に用いた場合、導電剤は不要になる。また比重は２．２で黒鉛と同じである。BC_3を構成するほう素（Ｂ）は、２Ｓ軌道に２個、２Ｐ軌道に１個の電子を持ち、炭素は２Ｓ軌道に２個、２Ｐ軌道に２個の電子を持つ。したがって炭素に比べて電子が１個欠乏している。

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【０００７】ここでBC_3正極を非水電解液中で充電すると導電性高分子ならびに炭素材料同様に、正極中にアニオンが吸蔵され、放電すると、吸蔵されたアニオンが電解液中に放出される。そしてそのときの平均放電電圧は、Ｌｉ極に対して４．５Ｖで放電容量も２１０ｍＡｈ／ｇとなる。このように正極にBC_3を用いることで、高容量で高電圧な非水電解液二次電池を提供できることとなる。
【０００８】
【実施例】以下本発明の実施例を説明する。
（実施例１）BC_3の電極としての特性を検討するため、図１に示すコイン型の非水電解液二次電池を作った。
【０００９】まず$BC_3$１０ｇに対して結着剤としてポリ４フッ化エチレン１ｇを混合して合剤とした。この合剤０．１ｇを直径１７．５ｍｍに加圧成型してBC_3極１とし、ケース２の中に置いた。微孔性ポリプロピレンセパレータ３をBC_3極１上に置いた。１モル／１の過塩素酸リチウム（$LiClO_4$）を溶解したプロピレンカーボネート（ＰＣ）を非水電解質としてセパレータ３上に注液した。この上に、内側に直径１７．５ｍｍの金属Ｌｉ４を張り付け、外周部にポリプロピレンガスケット５を付けた封口板６を置いて封口し、コイン型の非水電解液二次電池を作製した。
【００１０】つぎに２ｍＡの定電流で、BC_3電極１がＬｉ対極４に対して４．７Ｖになるまでアノード分極（BC_3電極を正極として見る場合には充電に相当）し、次にBC_3電極１が３．０Ｖになるまでカソード分極（放電に相当）した。そしてこのアノード分極、カソード分極を繰り返し行なった。
【００１１】従来例として、気相成長法炭素材料ならびにポリアニリンを用いて、BC_3電極と同様に電極を作製し、次に同じように試験セルを作りアノード分極、カソード分極を繰り返し行なった。以後気相成長法炭素材料ならびにポリアニリンを用いた電極をＣ電極、Ｐ電極と略す。なおＰ電極に関しては、Ｌｉ対極に対して４．０Ｖになるまでアノード分極（正極として見る場合には充電に相当）し、次にＰ電極が３．０Ｖになるまでカソード分極（放電に相当）した。そしてこのアノード分極、カソード分極を繰り返し行なった。
【００１２】正極にBC_3電極、Ｃ電極、Ｐ電極を用いた非水電解液二次電池の１サイクル目の充放電曲線を図２に示す。また（表１）に初期放電容量、初期放電容量に対する１００サイクル目の非水電解液二次電池の放電容量の容量維持率を示す。
【００１３】
【表１】

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正　　極	放電容量（ｍＡｈ／ｇ）	１００サイクル目の放電容量維持率（％）
BC_3	２１０	９７
Ｃ	７５	９２
ポリアニリン	１４８	８９

【００１４】放電電圧はBC_3電極を正極として用いたものが、Ｃ電極ならびにＰ電極を用いたものより高く、また電気容量も本実施例のBC_3電極を用いたものが２１０ｍＡｈ／ｇと大きいことがわかった。また１００サイクル目の放電容量維持率もBC_3電極を用いたものが最も高い値を示した。

（実施例２）本実施例では、高温保存特性について調べた。

【００１５】BC_3を正極とする図１に示すコイン型の非水電解液二次電池を構成した。また従来例として、気相成長法炭素材料ならびにポリアニリンを用いて、BC_3電極と同様にＣ電極、Ｐ電極を正極としたコイン型の非水電解二次電池を作製した。前記電池の作製法は実施例１と同様の方法で行った。

【００１６】非水電解液二次電池の高温保存試験は、次の方法で行った。２０℃、２ｍＡの定電流でBC_3電極、Ｃ電極を用いたものに関しては、４．７Ｖまで、Ｐ電極を用いたものに関しては、４．０Ｖまで充電し、次にいずれの非水電解液二次電池も３．０Ｖまで放電し、この充放電を５サイクル行い、６サイクル目の充電が終わった後、６０℃で３週間保存した。保存後２０℃に戻して、同条件で放電した。ここで容量維持率は次のように定義した。

【００１７】容量維持率＝１００×６サイクル目の放電容量／５サイクル目の放電容量

また保存終了後に充電を行い、その後の放電容量を評価した。ここで容量回復率を次のように定義した。

【００１８】容量回復率＝１００×７サイクル目の放電容量／５サイクル目の放電容量

（表２）に各非水電解液二次電池の３週間後の容量維持率、容量回復率を示す。

【００１９】

【表２】

正　　極	５サイクル目放電容量（ｍＡｈ／ｇ）	容量維持率（％）	容量回復率（％）
BC_3	２０９	９０	９６
Ｃ	７４	８２	９３
ポリアニリン	１４５	６２	８５

【００２０】BC_3電極を用いた非水電解液二次電池が、容量維持率ならびに容量回復率がＣ電極、Ｐ電極を用いた非水電解液二次電池に比べて最も大きい。このように、本実施例の非水電解液二次電池は、BC_3電極を正極として用いたことにより、高い放電電圧、高容量、優れた保存特性を兼ね備えたことがわかった。

【００２１】なお各実施例ではコイン型の非水電解液二次電池で説明したが、円筒型、角型などの形状によって変わるものではない。

【００２２】

【発明の効果】以上の実施例の説明より明らかなように、本発明は充放電可能な正極と、非水電解液と、充放電可能な負極を具備する非水電解液二次電池において、前記正極にBC_3を用いたため、高エネルギー密度で、保存性に優れた二次電池を得ることができ、産業上の意義は大きい。

【図面の簡単な説明】

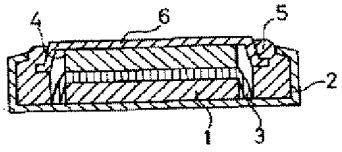
【図１】本発明の正極を使ったコイン型の非水電解液二次電池の断面図

【図２】従来例と比較した本発明の正極を用いたコイン型の非水電解液二次電池での充放電曲線図

【符号の説明】

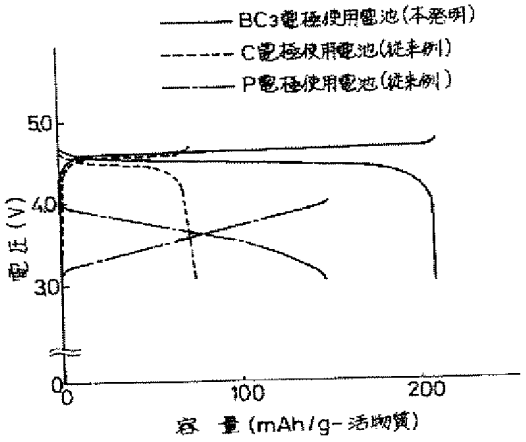
１　電極（正極）
２　ケース
３　セパレータ
４　金属Ｌｉ
５　ガスケット
６　封口板

【図１】



1----電　極(正　極)
2----ケース
3----セパレータ
4----金　属 Li
5----ガスケット
6----封口板

【図２】



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